

Amendments to the Specification

Please replace paragraph [0007] with the following paragraph:

[007] Coating macroporous supports using an intermediate mesoporous gamma-alumina sol layer prior to the deposition of a silica membrane has been attempted to overcome this problem of large pore defects. However, the quality of the sol layer is limited by, among other things, the size distribution of the sol particles. On the one hand, as depicted in Figure 1a), when a dipping solution is used consisting of sol particles that are large compared with the pore size of the supports, the particles do not provide additional restrictive passages for controlling selectivity. Additionally, they do not cover the surface uniformly and can leave patches of exposed, untreated surface. On the other hand, as depicted in Figure 1b) 2, if a dilute dipping solution is used consisting of sol particles that are small compared with the pore size of the supports, these small sol particles do not easily form “bridges” over some of the large features and extra large pores of the supports because of infiltration during dip-coating. Even if such “bridges” are formed, they are not strong and are easily broken or cracked. This problem becomes increasingly more serious for supports with broader pore size distributions.

Please replace paragraphs [0012]-[0028] with the following paragraphs:

[0012] For a more detailed description of the preferred embodiment of the present invention, reference will now be made to the accompanying drawings, wherein:

[0013] Figure 1a) is a schematic of a support with large sol particles placed thereon;

[0014] Figure 1b) 2-is a schematic of a support with small sol particles placed thereon;

[0015] Figure 2c) 3-is a schematic of a support with graded sol particles placed thereon, forming a uniform substrate layer, in accordance with a preferred embodiment;

~~[0016] Figure 4 is a schematic of a composite membrane in accordance with a preferred embodiment, including a support, a uniform substrate layer, and a silica layer;~~

~~[0017]~~[0016] Figure 2 5-is graph of particle size distributions of boehmite sols peptized with various acids;

~~[0018]~~[0017] Figure 3 6-is a graph of particle size distributions of boehmite sols peptized with acetic acid;

~~[0019]~~[0018] Figure ~~4~~ ~~7~~ is a graph of particle size distributions of boehmite sols hydrolyzed for various times;

~~[0020]~~[0019] Figure ~~5~~ ~~8~~ is a schematic of dip-coating machine for use in accordance with a preferred embodiment;

~~[0021]~~[0020] Figure ~~6~~ ~~9~~ is a graph of pore size distributions of gamma-alumina supports obtained from boehmite sols having various particle sizes;

~~[0022]~~[0021] Figure ~~7~~ ~~10~~ is a schematic of a suitable CVD apparatus for use in the deposition of the silica layer;

~~[0023]~~[0022] Figure ~~8~~ ~~11~~ is a graph of permeation properties at 873 K of an ungraded four layer silica/alumina membrane;

~~[0024]~~[0023] Figure ~~9~~ ~~12~~ is a graph of permeation properties at 873 K of a graded four layer silica/alumina membrane in accordance with a preferred embodiment;

~~[0025]~~[0024] Figure ~~10~~ ~~13~~ is a graph of permeation properties at 873 K of a graded five layer silica/alumina membrane in accordance with a preferred embodiment;

~~[0026]~~[0025] Figure ~~11~~ ~~14~~ is a graph of permeability of He, H₂, and Ne through a graded five-layer silica/alumina membrane in accordance with a preferred embodiment;

~~[0027]~~ Figure ~~15~~ is a low resolution electron micrograph of a graded five layer silica/alumina membrane prepared by the method described in Example 9; and

~~[0028]~~ Figure ~~16~~ is a high resolution electron micrograph of the graded five layer silica/alumina membrane prepared by the method described in Example 9.

Please replace paragraph [0030] with the following paragraph:

[0030] According to one preferred embodiment of the present invention, a porous support is dip-coated with a series of boehmite sols having sequentially decreasing particle size distributions. As depicted in Figure ~~1c~~ ~~3~~, this gives rise to a graded structure with satisfactory filling of voids, thereby avoiding (or at least minimizing) defects. In order to accomplish this task, sols having controlled particles size distributions are needed.

Please replace paragraphs [0034]-[0035] with the following paragraphs:

[0034] For some embodiments, the aluminum isopropoxide was hydrolyzed at 353 K for 24 hours and then peptized using acetic acid, nitric acid and/or hydrochloric acid, using a molar ratio of

$H^+/Alkoxide=0.10$ (Figure 2_5). It should be understood that the H^+ refers to the total normal equivalents of H^+ and not the hydronium ion concentration taking into account the K_a of the acid. For other embodiments, the aluminum isopropoxide was hydrolyzed at 353 K for 24 hours and then peptized using acetic acid using different molar ratios of $H^+/Alkoxide$ in the range of 0.03-0.25 (Figure 3_6). In still other embodiments, the aluminum isopropoxide was hydrolyzed at 353 K for 0.5, 3, 24 and 72 hours, and then peptized using acetic acid with a molar ratio of $H^+/Alkoxide=0.15$ (Figure 4_7). These sols characterized in Figures 2-4 5-7-remained stable for more than 3 months.

[0035] A dynamic light scattering analyzer (Horiba Model LB-500) was used to measure the particle size distribution of the sols. The concentration of the sols obtained in each of Figures 2-4 5-7-was in the range of 0.75-0.85 M, and the exact sol concentration was obtained by measuring the volume of the sol. As can be appreciated from comparing Figures 2-4 5-7, stable boehmite sols with particle sizes in the range of 10-1000 nm were produced by controlling the sol-gel process parameters such as acid type, acid concentration and hydrolysis time.

Please replace paragraph [0039] with the following paragraph:

The alumina support was dipped into the dipping solution and withdrawn after 10 seconds at a rate of 0.01 meter/second using a dip-coating machine, as shown in Figure 5_8. The dip-coated alumina support was dried in ambient air for 24 hours, and then placed in a furnace connected with a temperature controller. The support was heated to 923 K in air at a rate of 1 K/minute and calcined in air at 923 K for 2 hours. As described further below, the dipping-calcining process was repeated 3-5 times per support using either a single sol or a series of sols having sequentially smaller average particle sizes to form a uniform membrane substrate.

Please replace paragraph [0043] with the following paragraph:

[0043] The Barrett, Joyner and Halenda (BJH) method was used to determine the pore size distribution using the desorption isotherm. Figure 6_9-illustrates the pore size distributions of the gamma-alumina supports prepared from the boehmite sols containing particles of size of 630, 200, and 40 nm. These supports had a sharp pore size distribution. Additionally, Table 1 lists the microstructure parameters of these three supports. It was discovered that the larger the particle size

of the sols, the larger the pore size and porosity of the resulting membranes, as discussed in connection with Figure 1.

Please replace paragraphs [0045]-[0047] with the following paragraphs:

[0045] A suitable CVD apparatus is shown in Figure 7-40 and CVD process parameters are listed in Table 2. Briefly, the reactor assembly 210 for depositing the permselective membrane on the porous substrate 220 comprises an outer concentric, nonporous tubing 230 and a temperature-controlled heater 250. The porous substrate 220 is surrounded by outer concentric, nonporous tubing 230 of larger diameter, forming an annulus (not shown). The inside of the porous tubing 220 is referred to herein as the "tube" side 262 whereas the outside of the porous tubing 220 that is located inside the outer concentric, nonporous tubing 230 is referred to as the "shell" side 264. The concentric tubing 220 and outer concentric, nonporous tubing 230 are located in temperature-controlled heater 250.

[0046] A CVD reactant gas is generated by a gas dilution system 310 as depicted in Figure 7-40. As used herein, the term CVD reactant gas refers to the gas or gases being deposited in the CVD process. As used herein, the term CVD gas stream refers to the CVD reactant gas as well as any associated inert carrier gases.

[0047] Referring still to Figure 7-40, carrier gas from carrier gas cylinder 320 passes through a temperature-controlled bubbler 330 containing the liquid CVD material 334. In some embodiments, the carrier gas passes through an oxygen-water trap 322 prior to entering temperature-controlled bubbler 330. The carrier gas saturated with CVD reactant gas then flows through a tee 340, in which it is mixed with dilution gas flowing from a dilution gas cylinder 350. In some embodiments, the carrier gas saturated with CVD reactant gas passes through an oxygen-water trap 342 prior to mixing in dilution gas cylinder 350. The mixed gas stream containing the CVD reactant gas, carrier gas and dilution gas then passes into the upstream end 272 of the tube side of the porous tubing, through the porous tubing, and out the downstream end 274 of the tube side of the porous tubing. The concentration of the CVD reactant gas in the CVD gas stream can be varied considerably and accurately by adjusting the temperature of the bubbler 330 as well as the mass flow controllers 312 located downstream of the carrier gas cylinder 320 and the dilution gas cylinder 350.

Please replace paragraph [0053] with the following paragraph:

[0053] Figure 2_5 shows the particle size distributions of the three boehmite sol solutions obtained with the corresponding acids. It can be seen that the sols prepared with inorganic acids have smaller average particles sizes than the sols prepared with acetic acid. The boehmite sol peptized with nitric acid was found to have a median particle size of 55 nm and was designated BS55. BS55 was used for the preparation of the intermediate layers of gamma-alumina in membrane substrates, later described.

Please replace paragraph [0054] with the following paragraph:

[0054] Boehmite sols were prepared using the method described in Example 1, except the hydrolyzed solution was peptized with various quantities of acetic acid to give molar ratios of $H^+/Alkoxide$ of 0.03, 0.04, 0.055, 0.07, 0.10, 0.15 and 0.25. Figure 3_6 shows the particle size distributions in these seven boehmite sol solutions. When acetic acid was used as the peptizing agent, the median particle size of the resulting boehmite sols increased from 65 nm to 950 nm with decreasing molar ratio of $H^+/Alkoxide$ from 0.25 to 0.03. Thus, lower acetic acid concentration tends to favor the formation of larger particles. The two boehmite sols which were peptized with acetic acid at molar ratios of $H^+/Alkoxide$ of 0.04 and 0.07, and which had median particle sizes of 630 and 200 nm, respectively, were designated as BS630 and BS200. BS630 and BS200 were also used for the preparation of the intermediate layers of gamma-alumina in membrane substrates, later described.

Please replace paragraph [0055] with the following paragraph:

[0055] Boehmite sols were prepared using the method described in Example 1, except the aluminum isopropoxide was hydrolyzed at 353 K for various times (0.5, 3, 24 and 72 hours) and the solution was peptized for 20 hours with acetic acid at a molar ratio of $H^+/Alkoxide$ of 0.15. Figure 4_7 shows the particle size distributions in these boehmite sol solutions. As the hydrolysis time increased from 0.5 hours to 72 h, the median particle size of the resulting boehmite sols increased from 13 nm to 120 nm. The boehmite sol which was hydrolyzed at 353 K for 3 hours and peptized with acetic acid at a molar ratio of $H^+/Alkoxide$ of 0.15 and which had a median particle size of 40 nm was designated as BS40. BS40 was used for the preparation of the immediate layers of gamma-alumina in membrane substrates, later described.

[0061] A similar procedure was used to prepare a membrane substrate using dipping solution DS630. This was designated membrane substrate 630-630-630-630. The permeation properties of membrane substrate 630-630-630-630 are shown in Figure 8 and are also listed in Table 3.

Please replace paragraph [0063] with the following paragraph:

[0063] The same method was used as in Example 5, except the four dipping-calcining steps were carried out with different 0.15 M dipping solutions in the order DS630, DS630, DS200 and DS40. As described in Example 4, the solutions DS630, DS200 and DS40 contained the sols with median particle sizes of 630, 200 and 40 nm, respectively. First, the support was dipped in the dipping solution DS630, dried and then calcined as described in Example 5. Then, the dipping-calcining procedure was repeated using the same dipping solution DS630, followed by application of the dipping-calcining procedure with solutions DS200, and DS40. This membrane substrate was designated membrane substrate 630-630-200-40. The pore size distribution of membrane substrate 630-630-200-40 is given in Figure 6-9 and the permeation properties are listed in Table 4.

Please replace paragraph [0066] with the following paragraph:

[0066] The CVD process was conducted for 3 hours and 6 hours with the apparatus shown in Figure 7-10 and the process parameters listed in Table 2. The permeation properties of the resulting composite membranes at 873 K before and after CVD are listed in Tables 5 and 6.

Please replace paragraphs [0068]-[0069] with the following paragraphs:

[0068] This example describes the preparation of a silica membrane utilizing a membrane substrate with four multiple graded layers. The membrane consists of a thin silica layer deposited by CVD on top of a membrane substrate obtained in Example 6 (*i.e.* using dipping solutions DS630, DS630, DS200 and DS40). A silica layer was deposited on an intermediate gamma-alumina layer, which was obtained by sequentially dipping-calcining sols with particle size of 630, 630, 200 and 40 nm.

[0069] The silica layer was deposited by the CVD of TEOS at high temperature as described in U.S. Patent 6,527,833, in a similar manner as in Example 7. The CVD process was conducted for 5 hours with the process parameters listed in Table 2. The permeation properties of the resulting

membrane at 873 K before and after CVD are listed in Table 7 and are graphically shown in Figure 9-12.

Please replace paragraphs [0071]-[0072] with the following paragraphs:

[0071] This example describes the preparation of another silica membrane prepared using a membrane substrate with five graded layers. The membrane had a thin silica surface layer deposited by CVD, similarly to Examples 7 and 8. A silica layer was deposited on an intermediate gamma-alumina layer, which was obtained by sequentially dipping-calcining sols with particle size of 630, 630, 200, 40 and 40 nm.

[0072] The substrate in this case was one of the membrane substrates described in Example 6 which had five graded layers of different particle-sized gamma-alumina on a porous alumina tube (*i.e.* using sequentially dipping solutions DS630, DS630, DS200, DS40 and DS40). The CVD of TEOS was conducted for 3 hours with the process parameters listed in Table 2. The permeation properties of the resulting membrane at 873 K before and after CVD are listed in Table 8 and graphically shown in Figure 10-13.

Please replace paragraphs [0074]-[0077] with the following paragraphs:

[0074] This example illustrates the unique permeability properties of a silica membrane using graded substrates in accordance with a preferred embodiment of this invention. A composite membrane with a five-layer substrate similar to the one described in Example 9 was prepared with freshly synthesized sols as described in Examples 1 and 2. The median particle sizes of the sols were 630, 630, 200, 40, and 40 ~~540, 540, 170, 40, 40~~ nm, producing a membrane 630-630-200- 40- 40 ~~540-540-170-40-40~~.

[0075] The permeability of the membrane for He, H₂, and Ne was measured and the results are presented in Figure 11-14. In Figure 11-14, the permeability of the membrane rises with temperature, as expected. The almost complete exclusion of CO₂, CO, and CH₄ (Table 8) can be understood from the large size (> 0.3 nm) of these species (see Table 9).

[0076] Looking still at Figure 11-14, the permeation properties of the membrane appear to be those of the silica layer, as it was already demonstrated that the porous substrate permitted the permeation of the larger species in Examples 7-9.

[0077] However, the order of permeability, $\text{He} > \text{H}_2 > \text{Ne}$, is unexpected because it follows neither the size nor weight of the species; generally, porous materials allow faster passage of smaller species or lighter species. Comparing Table 9 with Figure 11-14, He is heavier than H_2 , yet permeates faster. Ne is smaller than H_2 , yet permeates slower. Without wishing to be bound by any particular theory, the order and behavior of the species appears to be explained by a solubility site mechanism for permeation originally derived to describe permeation in vitreous glasses (J. S. Masaryk, R. M. Fulrath, *J. Chem. Phys.* **59** (1973) 1198). The governing equation for the solubility site mechanism is:

$$Q = \frac{1}{6L} \left(\frac{d^2}{h} \right) \left(\frac{h^2}{2\pi m k T} \right)^{\frac{3}{2}} \frac{(N_s / N_A)}{(e^{h\nu^*/2kT} - e^{-h\nu^*/2kT})^2} e^{-\Delta E_k / RT} \quad [4]$$

Please replace paragraphs [0082]-[0083] with the following paragraphs:

[0082] ~~Figures 15 and 16, respectively, are low- and high-resolution electron micrographs of an exemplary five-layer composite membrane 630-630-200-40-40 exhibit the properties described herein. Referring first to Figure 15~~ In a low-resolution micrograph, the bottom portion of the micrograph shows the coarse structure of the porous support, while the top portion shows the 5-layer substrate. ~~The boundary-boundaries between layers is-are not discernible, partly because only 3 sol sizes (630, 200, 40) were used. Close inspection shows the particles at the top are smaller than those at the bottom.~~

[0083] ~~Referring now to Figure 16, the~~ A high-resolution micrograph of the same membrane shows the topmost part of the membrane formed by the sols of size 40 nm. Careful examination reveals a thin layer at the very top with a slightly different contrast than the alumina particles. This is the silica layer, of thickness 10-20 nm.